

C455A - Homework 8 -- Due *Tues May 27* at 5PM

**Text Problems (Work in the order given below):**

**Q11.4**

**Q11.7**

**P11.3** - Hund's rules for ground states of H through F

**P11.4** – Energy difference between singlet and triplet

**P11.33** – Quantum numbers for terms

**Q12.17** -- Justification of Born-Oppenheimer

**P12.2** -- Overlap integral for various effective orbital sizes

**Q12.7** –  $H_{aa}$  interpretation

**Additional Problems**

1) Without using equations, explain each of the 3 Hund's rules discussed in lecture for ranking terms and levels.

2) "Atomic Units" You may have noticed many of our equations are accumulating a large number of complicated constants that appear repeatedly. For instance, the Bohr Radius:

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2}$$

Many of our equations can be made simpler by "giving up" SI units, and working in units more suited to the problem at hand, then "converting back" to SI units at the end (it can save you from dropping that darn factor of  $h$  in the derivative and so on). If we pick any set of units, we might pick a set where  $\hbar=1$ , the electron mass = 1, the electron charge = 1, and the permittivity of free space,  $4\pi\epsilon_0 = 1$ . If we work in such "atomic units" (theorists do) then the formula for the

allowed energy levels for a Hydrogen-like atom with nuclear charge  $Z$  becomes just:  $E = \frac{Z^2}{2n^2}$

where the units are given in "hartrees" (after the Hartree in Hartree-Fock).

**A)** How many eV are in 1 hartree? How many J?

**B)** Variational treatment of He atom ("Lite version:" We will take much of the math work and leave only a few steps the end for you to do):

In atomic units the Hamiltonian of He is  $H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$

**C)** Write out a trial wavefunction of the form  $1s(1)1s(2)$  and show that in atomic units it has the form:

$$\Psi(r_1, r_2) = \frac{Z^3}{\pi} e^{-Z(r_1+r_2)}$$

where  $r_1$  and  $r_2$  are the radial positions of the two electrons. We can use the variational theorem to minimize the energy by varying  $Z$ .

If you evaluated  $\langle E \rangle = \int \int \Psi^*(r_1, r_2) \hat{H} \Psi(r_1, r_2) dr_1 dr_2$  you would, after a lot of math come to:

$$\langle E \rangle = -Z^2 + \frac{2(Z-2)Z^3}{\pi} \int_0^\infty \frac{e^{-2Zr}}{r} 4\pi r^2 dr + \frac{5}{8} Z$$

**D) Complete the evaluation of this integral, and then find the value of  $Z$  that minimizes  $E$ . Your value of  $E$  will be in Hartrees.**

**E) Compare this value of the total energy of the He atom with the value you would get by assuming each electron occupied a normal hydrogen-like 1s orbital around a nucleus of charge  $Z$  (ignoring e-/e- repulsion, and also with the experimental value of  $-79.0$  eV. Is this result consistent with the variational theorem?**

**F) Why does the calculation not match the experimental energy (i.e. what real effect has our calculation ignored?)**

**G) Interpret the value of  $Z$  that minimizes  $E$ .**